

# PATENT SPECIFICATION

828,791



Date of Application and filing Complete

Specification: November 29, 1955. No. 34154/55

Application made in Italy on December 3, 1954 ←

Application made in Italy on December 16, 1954

Complete Specification Published: February 24, 1960

Index at Acceptance:—Classes 1(1), A3B1; and 2(6), P7D(1X:2A1:2B:3), P7FX, P7P1(A:B:C:F:X),

P7P(3:5), P7P6(A-G:Y), P7T1(C:Y)

PATENTS ACT, 1949

SPECIFICATION NO. 828,791

The following incorporates the correction of clerical errors in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated

Page 3, line 71, after "porcs" insert "or"

Page 4, line 120, for "producs" read "produces"

Page 5, line 9, for "TiC1<sub>4</sub>" read "TiCl<sub>4</sub>"

Page 6, line 28, for "cromium" read "chromium"

Page 6, line 58, for "structuure" read "structure"

Page 7, line 35, for "sulphur" read "sulfur"

Page 7, line 39, for "lyophilio" read "lyophilic"

Page 7, line 40, for "redicals" read "radicals"

Page 7, Table VI, for "Al treheral" read "Al trihexyl"

Page 8, line 15, for "obtainened" read "obtained"

Page 9, line 15, for "tetralinisonaphalene" read "tetrahydronaphalene"

Page 10, line 42, for "98°C." read "90°C."

Page 10, line 65, after "92" insert "2, propylene are added and the autoclave is"

Page 11, delete line 1"

Page 14, line 44, for "crystalline" read "crystalline"

Page 15, line 73, for "correseponding" read "corresponding"

Page 17, line 35, for "0.012 moles" read "0.02 moles"

Page 18, line 5, for "150" read "2150 ml."

Page 19, line 103, for "proportins" read "proportions"

Page 19, line 111, for "Group IV" read "Group IVa"

Page 20, line 36, for "is in" read "is a"

Page 20, line 76, for "32" read "23"

THE PATENT OFFICE,

28th February, 1961

for example, by stretching to form threads having valuable properties.

These linear, essentially unbranched, head-to-tail polymers are unique of their kind. Both the crystalline and amorphous types of polymers are linear, as shown by their infra-red spectra. Thus, for example,

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um, or with a complex hydride or a complex organo-metallic compound or boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal of Group IVa, Va or VIa is present in the

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PATENTS ACT, 1949

SPECIFICATION NO. 828,791

The following incorporates the correction of clerical errors in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the thirtieth day of May, 1960, and the amendment under Section 29 of the Patents Act, 1949, in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the twentieth day of September, 1960:—

Page 3, line 119, for "filtration" read "extraction".

Page 13, line 61, for "fractioned" read "fractionated"

Page 20, line 78, for "prevailingly" read "predominantly"

Page 11, line 16)

Page 12, line 60)

Page 14, line 72, for "crystallinity" read "crystalline"

Page 17, line 27)

Page 17, line 93)

Attention is also directed to the following Printer's Error:—

Page 1, line 1, after "Generale" insert "Per"

Page 1, line 35, after "solid" insert "comma"

Page 1, line 49, after "known" insert "branched"

Page 1, line 61, after "These" delete "comma"

Page 1, line 64, for "part" read "parts"

Page 1, line 81, for "or" read "of"

Page 2, line 20, for "ilsable" read "lisable"

Page 2, line 110, for "cataylist" read "catalyst"

Page 3, line 7, for "cystalline" read "crystalline"

Page 3, line 42, for "non-chystallisable" read "non-crystallisable"

Page 3, line 49, for "filtrate" read "filtrate"

35 crystallisable elastomer, whilst the solid highly crystalline polymers can be oriented, for example, by stretching to form threads having valuable properties. These linear, essentially unbranched, 40 head-to-tail polymers are unique of their kind. Both the crystalline and amorphous types of polymers are linear, as shown by their infra-red spectra. Thus, for example, of aluminium or alloy or with an hydride or organo-metallic compound of the said metal of Group Ia or II and/or of aluminium, or with a complex hydride or a complex organo-metallic compound or boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal 85 of Group IVa, Va or VIa is present in the

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International Classification:—B01j. C08f.

## COMPLETE SPECIFICATION

### DRAWINGS ATTACHED

#### Method of Selectively Polymerising Alpha-olefins

We, MONTECATINI SOCIETA GENERALE L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 18 Via Filippo Turati, Milan, Italy, and KARL ZIEGLER, a German citizen, of Kaiser-Wilhelm-Platz 1, Muelheim-Ruhr, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for the selective polymerisation of alpha-olefins of the general formula  $\text{CH}_2=\text{CHR}$  (where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group).

In the Specification of patent application No. 16362/55 (Serial No. 810023) new linear, essentially unbranched, head-to-tail polymers of unsaturated hydrocarbons of this same general formula and methods for the production thereof are described and defined. As disclosed in said patent application, mixed linear, essentially unbranched, head-to-tail polymers are obtained which contain amorphous and crystalline parts in various and unregulated proportions. These polymers show very different properties, depending upon their steric structure and their molecular weight. The amorphous polymers have viscous-elastic properties, which lie between those of a highly viscous fluid and those of a non-vulcanised, non-crystallisable elastomer, whilst the solid highly crystalline polymers can be oriented, for example, by stretching to form threads having valuable properties.

These linear, essentially unbranched, head-to-tail polymers are unique of their kind. Both the crystalline and amorphous types of polymers are linear, as shown by their infra-red spectra. Thus, for example,

the infra-red spectra of the polypropylenes produced according to the invention of Application No. 16362/55 (Serial No. 810023), i.e. both of the crystalline and the amorphous types, were quite different from the infra-red spectra of known polypropylenes. Prior to the date of said application only one example was known of a type of vinyl polymer which existed in both amorphous and crystalline forms; this type comprised the polyvinyl ethers described by Schildknecht and collaborators (Ind. Eng. Chem., Vol. 40 (1948), Page 2104, and Vol. 41 (1949) page 1998). These polyvinyl ethers are, of course, completely different from the polymerisation products of the said application.

These, linear, essentially unbranched, head-to-tail polymers with unregulated proportions of crystalline or crystallisable to non-crystallisable part may be produced according to the specification of patent application No. 16362/55 (Serial No. 810023) by a method of polymerising an alphaolefin of the said general formula  $\text{R-CH=CH}_2$  or a mixture of such alpha-olefins, either alone or with ethylene and/or other hydrocarbon having at least one vinyl double bond, wherein there is used a catalyst formed by contacting an halide (other than a fluoride) of a metal of Group IVa, Va or VIa of the Periodic Table as therein defined, with a metal of Group Ia or II of the said table or aluminium or alloy or with an hydride or organo-metallic compound of the said metal of Group Ia or II and/or of aluminium, or with a complex hydride or a complex organo-metallic compound or boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal of Group IVa, Va or VIa is present in the

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catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen-free conditions polymerisation of the said olefin or hydrocarbon mixture results.

The term "linear, essentially unbranched" is defined in the said specification as meaning that the main polymer chain has no branches substantially longer than R and this term has the same meaning in the present specification and the claiming clauses hereof. Likewise Groups Ia, II, IVa, Va and VIa are defined in the said specification and have the like meanings herein and in the claiming clauses hereof.

We have now found that in processes for the polymerisation of many alpha-olefins it is possible to regulate the proportions of crystalline or crystallisable to non-crystallisable linear, essentially unbranched, head-to-tail polymer formed in the polymerisate, by control of the catalyst.

The present invention is thus in part a modification of the method disclosed in the specification of Application No. 16362/55 (Serial No. 810023) and provides a method of polymerising an alpha-olefin having at least three carbon atoms which satisfies the general formula  $R-CH=CH_2$  (where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group), to form a linear, essentially unbranched, head-to-tail polymer by the use as a catalyst of a compound of a metal of Group IVa, Va or VIa as hereinafter defined, in contact with metal-alkyl groups containing aluminium or a metal of Group II as hereinafter defined, at least a part of the metal of Group IVa, Va or VIa being present in the catalyst in a valency state lower than the maximum, wherein the crystallisable or non-crystallisable content of the polymerisate is selectively regulated towards an increased crystallisable or non-crystallisable content, as the case may be, by the respective use in the polymerisation process of a said catalyst in the wholly or substantially wholly solid form, or in the wholly or substantially wholly non-solid form, the appropriate form resulting either directly from a suitable choice of starting materials and conditions of formation or from an intermediate step of preparation to produce a catalyst having a selected proportion of the solid to the non-solid form, the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen free state polymerisation of the said olefin to a linear, essentially unbranched, head-to-tail polymer results.

By the expression "in contact with" we mean bonded to or otherwise associated with, as in a complex. We believe that in the case of solid catalysts, complexes may exist only on the surface of the heavy metal com-

pound. The phrase "in contact with" used herein and in the claiming clauses hereof is to be understood in this sense.

It will be understood that the crystallisable content of the polymerisate may, under suitable conditions, be present in the wholly or partly crystalline state and the word "crystallisable" as used herein and in the claiming clauses hereof in relation to the polymerisate includes a content in a wholly or partly crystalline form.

By the term "solid" when used herein and in the claiming clauses hereof in respect of the catalyst we mean in the form which is not soluble or capable of micellar dispersion in any hydrocarbon used in the polymerisation process and by the term "non-solid" used in respect of the catalyst we likewise mean in the form in which it is or may be dissolved or dispersed in micellar state in a hydrocarbon used in the polymerisation process.

The proportion of crystalline or crystallisable polymer formed in the polymerisate is increased if the catalyst is in the solid form and is insoluble in the reaction medium (olefin or olefin and solvent) and one manner of achieving this result is to use as one of the starting substances for the production of the catalyst, an insoluble heavy metal compound in which the heavy metal is already present in a lower valency than the maximum valency which the said metal can have according to its place in the Periodic Table. For example, it is possible to start from solid, crystallised titanium dichloride or titanium trichloride and to control the production of the catalyst in such a way that the catalyst consists of solid parts in contact with metal alkyl groups.

On the other hand, the proportion of non-crystallisable polymer formed in the polymerisate may be increased, or in certain cases a wholly or substantially wholly non-crystallisable polymerisate formed if the catalyst is in the non-solid state. If a solid, heavy metal compound is used as one of the starting substances for the production of a non-solid catalyst, care must be taken to ensure that the compound is adequately dispersed, for example, by use of metal alkyl compounds containing long alkyl groups, when the catalyst is made. When liquid titanium tetrachloride is used as the heavy metal compound, care should be taken to ensure that the reduction takes place under such circumstances that no solid part forms, or, if it forms, that the solid part is kept to the minimum.

For the purposes of this specification and of the claiming clauses hereof the definition of a metal of the aforesaid groups is as follows:—

- Group Ia—Li, Na, K, Rb, Cs.  
 " II —Be, Mg, Ca, Sr, Ba, Zn, Cd.  
 " IVa—Ti, Zr, Hf, Th.  
 " Va—V, Nb, Ta.  
 5 " VIa—Cr, Mo, W, U.

Of the metals in Groups IVa, Va and VIa, we have found that solid, crystalline titanium, zirconium and vanadium compounds in a low valency state are particularly effective in the production of crystalline or crystallisable polymers.

Also for the purposes of this specification and of the claiming clauses hereof we exclude all fluoride compounds of metals of Groups IVa, Va and VIa and all references hereinafter to halides, oxyhalides or alkoxyhalides are to be understood as exclusive of fluorides, oxyfluorides and alkoxyfluorides.

It has further been found that catalysts such as are described in the Specification of patent application No. 16362/55 (Serial No. 810023) can be split up into fractions, of which the solid fraction, when used as a catalyst for the polymerisation (if desired with an additional amount of organometallic compound) results in the formation of an increased proportion of crystalline or crystallisable polymer in the polymerisate, whilst the non-solid fraction results in the formation of an increased proportion of non-crystallisable polymer in the polymerisate.

The solid part or fraction of the catalyst can, for the enhanced production of crystalline or crystallisable polymer, be prepared or increased by a known method, for instance by separating the solid fraction by filtration, decantation, sedimentation, centrifuging, or other suitable method, only coarser parts retained thereby (left on a filter, for example) being used.

On the other hand, for enhancing the production of non-crystallisable polyolefins, catalysts may be used, the non-solid part of which has been increased by a known method, for example, by separation, filtration, decantation, sedimentation, centrifuging or other suitable method, into solid and non-solid fractions only the non-solid parts (e.g. the filtrate) being used for polymerisation.

Whereas the unfractionated catalyst according to the Specification of patent application No. 16362/55 (Serial No. 810023) merely gives unregulated polymerisation to a polymer having an unselectively regulated proportion of crystalline or crystallisable to non-crystallisable parts, the separation of the catalyst into fractions in accordance with one embodiment of the present invention, as, for example, by filtration of a solution containing the catalyst through filter plates having relatively small pores, makes possible the use of the filtrate for the purpose of increasing the proportion of non-crystallisable polymer in one polymerisate and the use of

the filter residue for increasing the proportion of crystalline or crystallisable polymer in another polymerisate. For this purpose, it is advisable to use filters, for example porous glass or ceramic plates, which have pores 5 to 15 microns.

For the better understanding of the terms "crystalline", "crystallisable" and "non-crystallisable" as used in this specification in relation to the polymers produced in accordance with this invention, we append the following description of the manner in which the proportion of crystalline or crystallisable to non-crystallisable polymer formed in the polymerisate has been determined in the tables and examples which follow in this specification.

The polymerisate resulting from the method of the present invention was first examined by means of X-rays to determine the presence of crystalline parts in the polymerisate.

In cases where some crystallinity was shown, the polymerisate was extracted by means of the appropriate solvent (e.g. ether in the case of propylene or acetone in the case of butene) to dissolve all of that part of the polymerisate which gave no indication of crystallinity under X-rays, care being taken by the choice of the appropriate solvent or solvents and control through X-ray examination to prevent crystalline polymer passing into the filtrate.

The residue from the extraction by means of ethyl ether or acetone may in some cases be further divided into an extract and a residue by a further extraction with a suitable solvent, the characteristics of the residue in this second extraction being high crystallinity as determined by X-rays and a substantially constant melting point. By this is meant that if the residue is further extracted with solvents of higher dissolving power, the melting point of it will remain practically unchanged. By melting point is meant the temperature at which crystallinity wholly disappears.

This second separation into an extract and a residue also provides an extract which gives an indication of crystallinity when measured with X-rays, the extent of the crystallinity being, in the case of polypropylene, approximately 50%.

A suitable solvent for performing the second step of filtration is, in the case of polypropylene, boiling *n*-heptane. Other polyolefins produced by the invention may be likewise treated by either the same or other solvents.

We have regarded that residue which shows high crystallinity and a constant melting point to have 100% crystallisability, though this same residue may not be actually 100% crystalline but merely crystallisable (i.e. having a tendency to crystallise).

The extract from the said second step of extraction has this like tendency to crystallise but to a reduced extent.

This difference in properties of these residues and extracts of which crystallinity is one feature, is not due to differences of molecular weight, but is due to structural differences. We have inferred that this structural difference in the case of linear essentially unbranched, head-to-tail polymers of alpha-olefins of the general formula  $R-CH=CH_2$ , and which contain at least three carbon atoms, the polymers being made by the method of this invention, arises from the different relative orientation in space of the substituents bound to the asymmetric carbon atoms in the main chain of the molecules of the polymer.

One method of visualising these differences is to regard the main chain of carbon atoms of a molecule of the polymer as being represented as a zig-zag form on a plane surface (see Figure 1 of the accompanying drawings). Then for every R-group attached to an asymmetric carbon atom there are two possible orientations, one being when the R-group is considered as lying above the plane surface and the other when the R-group is considered as lying below that surface. If the arrangement of R-groups in the molecule is such that they may, at least in long stretches of the molecule, all be considered as located on one side of the plane surface, then the asymmetric main chain carbon atoms will all have the same steric configuration. Molecules in which the R-groups are arranged in this way, have a strong tendency towards crystallisation as confirmed by X-ray analysis.

We have found it convenient to refer to such polymers, the macromolecules of which are arranged as aforesaid, as "isotactic polymers" and to refer to polymers produced by this invention, the macromolecules of which have a random arrangement, as "atactic polymers". Polymers with such random arrangement in which R is larger than the hydrogen atom do not show a tendency to crystallise.

The representation of the chains in one plane is only referred to for purposes of simple explanation. In actual fact it is believed by us that in the case of isotactic polymers, the main chains do not assume a plane but a helicoidal structure in which the pitch of the helix corresponds with a specific number of monomeric units, which, for example, for polypropylene, polybutene and polystyrene, is three. In such cases it is believed that all bonds between R-groups and the main chains have the same angle of inclination towards planes normal to the axis of the helix as shown in Figure 2 of the accompanying drawings.

Isotactic polymers, apart from their tendency to crystallise, show a greater density, a higher softening point and a higher melting point and a lower solubility than the corresponding atactic polymer of the same molecular weight.

Crystallisability and isotacticity are related in as much as all isotactic polymers as herein defined are crystallisable though it appears from X-ray analysis that complete crystallisation of an isotactic polymer is not achievable (85% to 90% crystallisation probably representing the maximum practically obtainable from an isotactic polymer).

In the following tables and examples the percentage crystallisability of the polymer represents the amount, expressed as a percentage, of weight of crystallisable polymer in terms of the total polymer; the amount of crystallisable polymer being determined from the weight of the residue from the second step of extraction in conjunction with an X-ray evaluation of the amount of crystallisable polymer in the extract from the second step of extraction converted into percentage weight.

It will be observed that the present invention is concerned with polymers which are crystallisable by reason of regularity of configuration in the main chain tertiary carbon atoms. We are aware that it is possible to produce polymers of linear alpha-olefins which are crystallisable by reason of the length of the side chains and not by reason of the aforesaid isotactic structure. This side chain crystallinity may be recognised by X-ray examination, which detects the polymethylenic structure, true of linear paraffinic chains, similar to that of a low molecular weight polyethylene.

The present invention is not concerned with such polymers and we disclaim from the claiming clauses hereof any application of the present method to olefins the polymers of which are crystallisable by reason of the length of the side chains and not by reason of isotactic structure.

Table 1 shows the results of polymerisation with the aid of catalysts made from titanium tetrachloride or vanadium tetrachloride and aluminium triethyl, which, in the one case, were not fractionated, and in the other, were fractionated by filtration into the coarse solid residue and the finely dispersed filtrate. The table shows that, whilst the unfractionated catalyst produces a propylene polymerisate with a crystallisable content of 47.8%, fractionation gives, on the one hand a residue which when used as a catalyst leads to a polymerisate with a high (about 54%) crystallisability, and, on the other hand, a filtrate which yields an entirely amorphous polymer.

TABLE I

Percentage of crystallisability of polymerisates in polyolefins obtained by polymerisation of olefins in the presence of unfractionated or fractionated catalysts obtained from heavy-metal tetrachlorides and aluminium triethyl

Heavy-metal tetrachloride	TiCl <sub>4</sub>	VCl <sub>4</sub>
10 Polymerised hydrocarbon	Propylene	Styrene
Unfractionated catalyst	47.8	—
15 Fractionated catalyst:		
filter residue	53.7	68
filtrate	Completely amorphous	Completely amorphous

If the catalyst filter residue is again suspended and filtered in an inert fluid, a filtration residue is obtained which produces a polymerisation product with a still higher content of crystallisable polymer.

It will be understood that, as hereinafter mentioned, the said metal of Group IVa, Va or VIa is present in the catalyst in a valency state lower than the maximum, but this lower valency state may be achieved either by using as a starting material a compound in which the said metal is already in the lower valency state, or by the reduction in the valency state which occurs in the formation of the catalyst.

In the production of a polymerisation catalyst using a titanium compound with a lower valency, for instance where solid, powdered, micro-crystalline titanium dichloride or titanium trichloride is the starting substance, this is suspended in a hydrocarbon, and a metal alkyl compound such as triethylaluminium or diethylaluminium chloride is added, whereupon the mixture is heated to 50 to 90°C. If titanium trichloride be used as the starting substance, then the reaction mixture retains the same violet colour as the titanium trichloride itself. A solid catalyst is obtained which guides the polymerisation of unsaturated hydrocarbons essentially in the direction of the formation of polymerisation products of a crystalline or crystallisable structure. The proportion of crystallisable polymer in the product obtained is in general the higher, the purer the titanium trichloride used for the making of the catalyst, that is to say the lower its content of titanium tetrachloride and oxidation or hydration by-products thereof.

In place of titanium trichloride, it is possible in the example illustrated to start also from titanium dichloride, which is also suitable for the production of solid catalysts for a process which leads substantially to crystallisable polymerisation products of the alpha-olefins.

Titanium tribromide, on the other hand,

supplies, in spite of its valency and its crystalline, solid state of aggregation, larger quantities of non-crystallisable polymers than titanium trichloride. This is probably attributable to the fact that titanium tribromide is fairly soluble in the hydrocarbon used. The result is that when the reaction occurs with the organo-metallic compound a substantial part of the reaction compound is in the highly dispersed state and the catalyst which is produced by reaction of the dissolved titanium tribromide with the metal alkyl has a low content of solid form and is not substantially different from the catalysts which are produced from liquid or soluble halides (other than fluorides) of high valency.

If, on the other hand, heavy-metal compounds are used as the starting substance, in which the heavy-metal has a higher valency, in particular its maximum valency, for instance liquid titanium tetrachloride, then, even in the absence of dispersing agents, a smaller proportion of crystallisable polymer is obtained in the polymerisation product. The fact that some isotactic parts may still be contained in the polymerisate can be explained by the fact that a titanium compound of lower valency is contained in the black, solid precipitate which forms when titanium tetrachloride is reacted with the organo-metallic compound, the aforesaid titanium compound having, at least in part, a crystalline structure.

Titanium tetraiodide behaves similarly to titanium tetrachloride, in that it yields a catalyst having a relatively low proportion of solid form, thus producing predominantly non-crystallisable polymers. The relatively high melting point of titanium tetrabromide is of no effect here, since the titanium tetrabromide, under the conditions of the reaction, dissolves completely in the solvent used. These circumstances are confirmed by a study of Table II which shows the influence of the halogen bonded in the heavy-metal compound, wherein the halogen is bonded to the heavy-metal in both a lower as well as in a higher valency. The table gives the percentage crystallisability of polymers of propylene prepared with catalysts which were obtained by reaction of aluminium triethyl with a titanium trihalide or tetrahalide.

TABLE II

Propylene	TiCl <sub>4</sub>	TiBr <sub>4</sub>	TiI <sub>4</sub>
Tri-halide	85	44	10
Tetra-halide	47.8	42	46

It can be seen from the above Table that, in the case of bromide and iodide as the heavy-metal compound, the change in the valency from 4 to 3 does not produce any appreciable increase in the crystallinity of

the polymerisation product, because in these cases the degree of dispersion of the catalyst in the reagent in a non-solid form is decisive. Thus the catalyst which was obtained from titanium triiodide produces lower crystallisability than the catalyst produced from titanium tetraiodide, since the catalyst produced from titanium triiodide, is more finely dispersed in the reagent in a non-crystalline form than that obtained from titanium tetraiodide. In the case of titanium tribromide and titanium tetrabromide the various factors counterbalance themselves, for which reason the proportion of crystallisable substance in the polymerisation product is substantially the same in both cases. In the same way, the proportion of non-crystallisable to crystallisable constituents in the polymerisate formed can be influenced, to the advantage of the latter, by using compounds of another heavy-metal of Group IVa, Va or VIa of the Periodic Table, as herein defined, in a lower valency state than the metal can possess as a maximum valency by virtue of

its position in the Periodic Table. This is the case with compounds of zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium, for instance in the application of solid, crystalline vanadium trichloride, zirconium trichloride or chromium trichloride.

On the other hand, at least a predominantly or an exclusively non-crystallisable polymerisation product is obtained if, in the production of the catalyst there is used a heavy-metal compound of a metal named in the preceding paragraph in higher, especially in the maximum, valency, for example vanadium tetrachloride or vanadium oxytrichloride, zirconium tetrachloride or chromium oxydichloride. These relationships can be seen from Tables III and IV, showing the influence of the production of catalyst from heavy-metal chlorides of different valencies and aluminium triethyl, on the percentage crystallisability of the polymerisates obtained from propylene (Table III) and butene-1 (Table IV).

TABLE III

Valency	Ti	Zr	V	Cr	MoCl <sub>5</sub> /MoCl <sub>3</sub>
III	85	55	73	36.4	
IV	47.8	51.5	48		50
V			32.4		
VI				21	

TABLE IV

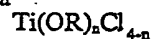
Valency	Ti	V
III	65	48.7
IV	51.5	27.8

The preferred embodiment of the invention using catalysts which are suitable for the formation of polymers of at least predominantly isotactic structure and consisting in the use of a solid, crystalline, low-valency state, heavy-metal compound as one of the starting substances, has numerous advantages as opposed to using other catalysts, for example, the possibility of using smaller quantities of organo-metallic compounds for the activation of the surface of the catalyst.

The substituents of the heavy-metal compound are of importance in the control of polymerisation. Both the chemical nature of the anions and the molecular magnitude thereof influence polymerisation, whereby as the magnitude of the anion, which is bonded to the heavy-metal, becomes greater, so the proportion of non-crystallisable polymeris-

ates increases.

If, as starting substances, titanium compounds or other compounds of other metals of Groups IVa, Va or VIa are used which, in addition to or in place of halogen atoms, contain lyophilic groups or other groups which interfere with crystallisation of the catalyst, for example alkoxy-groups or hydroxyl groups, such as in compounds of the general formula



in which n represents a number from 1 to 4, then, as the number of lyophilic or crystallisation-impeding groups increases, catalysts are produced, in the reaction with organo-metallic compounds, which have a less regular structure and a higher degree of dispersion and which therefore lead to the formation of atactic polymers. This can be seen from Table V, which shows the percentage crystallisability of polymerisation product obtained by polymerisation of propylene in the presence of catalysts produced from various titanium compounds of differing valency and different bonding, with aluminium triethyl.



TABLE V

Heavy-metal compound	State of heavy-metal compound at room temperature	% crystallisability
TiCl <sub>2</sub>	Crystalline solid	80-90
TiCl <sub>3</sub>	"	80-90
TiCl <sub>4</sub>	liquid	40
TiCl <sub>2</sub> (OR) <sub>2</sub>	"	35
TiCl(OR) <sub>3</sub>	"	10
Ti(OR) <sub>4</sub>	"	traces
Ti(OH) <sub>4</sub>	amorphous solid	"

The Table shows that, when titanium dichloride, which is both of the lowest valency and is also solid and crystalline, is used, a product of highest crystallisability is obtained. About the same results are obtained with titanium trichloride. With increasing valency, modification of the state of aggregation to liquid, and replacement of halogen atoms by alkoxy or hydroxyl groups, the percentage crystallisability in the polymerisable drops, whilst that of the non-crystallisable parts increases. With orthotitanic acid or tetra-alkyl titanates, exclusively atactic (non-crystallisable) products are obtained.

The formation of non-crystallisable polymerisation products may also be favoured by the use in the production of the polymerisation catalysts, of organic compounds of the metals of Groups II or III of the

Periodic Table, for example aluminium compounds, wherein the alkyl groups attached to the aluminium have increasing lyophilic properties. The presence of sulphur groups favours the degree of dispersion of the catalyst obtained. Micellar colloidal dispersions of the catalyst in the solvent are achieved. Suitable lyophilic groups for this purpose are alkoxy groups and, further, alkyl radicals with relatively long chains of carbon atoms, for example having more than 4 and preferably 6 to 16 carbon atoms.

Table VI shows the influence of the lyophilic groups in the organo-metallic component of the catalyst on the formation of crystallisable and non-crystallisable polymers in the polymerisation of propylene. In the Table is shown the percentage crystallisability.

TABLE VI

Propylene	TiCl <sub>2</sub>	TiCl <sub>3</sub>	TiCl <sub>4</sub>	Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Cl	Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	Ti(OH) <sub>4</sub>
Al triethyl	75	85	47.8	35.1	10	traces	traces
Al tripropyl		77.5	50.95		Ti(OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> 4%		
Al tributyl			30				
Al treheral		64	26.2				
Al trihexadecyl		59	16.2				

Table VI shows that the proportion of non-crystallisable polymers increases with the number of carbon atoms in the alkyl group of the aluminium trialkyl. Whereas the highest proportions of crystallisable polymers are obtained with aluminium triethyl, these proportions grow less as the alkyl chain becomes longer. Where aluminium alkyls with alkyl groups of considerable length and correspondingly high lyophilic properties are used, no crystalline precipitates are formed in reaction with

heavy-metal compounds, but only colloidal solutions. From these dispersions, the finely dispersed catalysts cannot be separated by mechanical processes such as filtration and the like.

It can be furthermore be seen from Table VI that the formation of non-solid catalysts and the degree of dispersion thereof can also be encouraged by the use of heavy-metal compounds which have alkoxy groups of considerable length. Thus dibutoxy-

titanium dichloride, even with aluminium-triethyl, leads to the formation of a catalyst which gives predominantly non-crystallisable polymerisates of unsaturated hydrocarbons.

The influence of the valency, too, of the heavy-metals, can also be seen from Table VI.

Table VII shows that the influence indicated in Table VI of the length of the alkyl chain in the organo-aluminium compound

is also present in heavy-metal compounds other than titanium compounds. In this Table is indicated the percentage of crystallisability of polymerisates, which have been obtained from propylene and butene-1 respectively, and catalysts which were produced from titanium, zirconium or vanadium tetrachloride or vanadium oxychloride or vanadium or chromium trichloride and aluminium alkyls of different chain lengths. 20

TABLE VII

	Propylene polymerisation						Butene-1 polymerisation
	TiCl <sub>4</sub>	ZrCl <sub>4</sub>	VC1 <sub>4</sub>	VC1 <sub>4</sub>	VoCl <sub>4</sub>	CrCl <sub>4</sub>	VC1 <sub>4</sub>
Al triethyl	47.8	51.5	48	54	32.4	36.4	27.8
Al tripropyl	50.95		41				
Al tridecyl		12				10	10
Al trihexadecyl	16.2				15		

The effect of the nature and the production of the catalyst on the polymerisation 30 can possibly be explained as follows.

It appears that the process may proceed thus—in the reaction of a solid, heavy-metal compound with organo-metallic compounds, complexes are produced, at least 35 superficially between the heavy-metal compound and the organo-metallic compound. The monomeric olefin adsorbed in the first place enters the alkyl chain at the surface of the catalyst, viz. on the heavy-metal side, whereby the alkyl chain grows. The paraffinic chain produced is less strongly 40 adsorbed at the surface of the catalyst than the monomeric olefin and tends to loosen itself from the surface of the catalyst. In like manner are a second and further molecules of the monomer adsorbed by the surface of the catalyst and incorporated in the metal alkyl chain. If the second and further 45 molecules of the monomer are oriented in the same way as the first molecule of the monomer, then a polymerisation product of regular structure and having a great tendency towards crystallisation will be obtained. This is the case where the catalyst 50 itself is solid and crystalline and presents a regular surface, as is the case with catalysts obtained by reaction of titanium trichloride with aluminium triethyl.

If the subsequent monomers are not 60 oriented, then an amorphous, non-crystallisable polymerisation (i.e. atactic) product will be obtained. This result is obtained when the surface of the catalyst cannot exercise any orienting action on account of 65 its non-solid structure, as is the case, for example, if the catalyst is present in micellar

dispersion in a solvent and presents no "orientation face" to the molecules of the monomer.

As with the process described in the 70 specification of application No. 16362/55 (Serial No. 810023) so with the present invention an alkyl compound of a metal of Group II. of the said table, or of aluminium, may be used in the formation of the cata- 75 lyst.

We have found that the polymerisation of many alpha-olefins may be regulated in the manner we have described and these include propylene, *n*-butene-1, *n*-pentene-1, 80 and styrene. We believe that in general alpha-olefins of the formula  $R-CH=CH_2$ , wherein R is as hereinbefore defined may be selectively polymerised in the manner described and particularly those in which R 85 is a linear alkyl group containing not more than 3 carbon atoms or an aryl group.

The following examples are given to illustrate the invention.

#### Example 1

90 Into a 2150 cc autoclave are introduced under nitrogen atmosphere two steel balls, a glass vial containing 7.2 g titanium dichloride and a solution of 11.4 g triethyl-aluminium in 500 cc *n*-heptane. The auto- 95 clave is then heated to 82°C, and at this temperature 140 g pure propylene are introduced, and the autoclave is then set in motion in order to break the vial, and kept in motion for about 10 hours at a tempera- 100 ture of 80-85°C; thereafter the gases are vented and the unpolymerized propylene is collected.

After pumping methanol into the auto- 105 clave, the polymer is taken out, as a white

powder, and is purified with acids to eliminate the inorganic products present. 115 g of a white powder are obtained, with a conversion of 82% on the used propylene.

- 5 The polymer obtained is fractionated by hot extraction with solvents.

The oily low molecular weight polymers, 5.8% of the obtained product, are removed by extraction with hot acetone. The following extraction with hot ether dissolves an amount of polymer, corresponding to 8.3% of the total polymer, which consists of solid polypropylene, amorphous under the X rays, having an intrinsic viscosity of 0.47 in tetralin isonaphthelene solution at 135°C.

- 15 By hot extraction with n-heptane a fraction is obtained, corresponding to 10.9% of the total; this fraction consists of polypropylene with an intrinsic viscosity of 0.57, and more than 50% crystallinity under the X rays. The extraction residue, corresponding to 75% of the total polymer, consists of a highly crystallisable, isotactic polypropylene having an intrinsic viscosity of 1.86.
- 20 The raw polymer obtained has therefore a crystallisability of at least 80%.

#### Example 2

- A glass vial containing 2 g  $\text{TiCl}_3$  in 30 ml n-heptane is introduced into a 435 ml autoclave together with a steel ball of 1 inch diameter (to break the vial at the moment the polymerization is to be started). A solution of 5.7 g triethyl-aluminium in 50 ml n-heptane is then introduced into the autoclave under nitrogen atmosphere and the autoclave is heated up to 70°C. At this moment 103 g of liquid propylene are admitted and soon afterwards the autoclave is put in motion in order to break the
- 30  $\text{TiCl}_3$  vial.

- A slight temperature increase is noticed, while the pressure decreases slowly but continuously. After 6 hours, during which time the temperature is kept between 80 and 90°C, when a pressure decrease is no longer observed, 50 ml methanol are pumped into the autoclave in order to decompose the catalyst, and the residual gases, containing 10 Nl of propylene, are released. From the autoclave a solid, compact mass is discharged, which is first purified with methanol and then with concentrated  $\text{HCl}$  while swelling the mass with boiling toluene. The product is then coagulated with methanol, filtered and washed with methanol and dried by heating under vacuum.

- 82 g of polymer are obtained, corresponding to a 79.6% conversion of the propylene employed. Said polymer is made up mostly (85%) of crystallisable, isotactic polypropylene, which may be separated from the non-crystalline products (15%) by extraction with solvents.

- 65 The amorphous portion is entirely soluble

in acetone; the greatest portion, soluble in warm ether, has a softening point of 100°C, an intrinsic viscosity of 0.685 and a molecular weight of about 18,000. The crystalline portion, insoluble in warm heptane, has a softening point of 165°C, an intrinsic viscosity 2.39 and a molecular weight of about 120,000.

#### Example 3

Into an oscillating 500 cc autoclave, fitted with a jacket for circulation of heating oil and provided with a control device for keeping the temperature constant within one degree, are introduced under nitrogen atmosphere 0.98 g  $\text{TiCl}_3$  and 220 cc anhydrous n-heptane. After evacuation, the solvent is saturated with pure propylene (98.5%) under a pressure of 1000 mm Hg above atmospheric pressure, at the same time bringing the temperature inside the autoclave to 70°C. The autoclave is kept in motion at 70°C for 90 minutes. Under propylene pressure a solution of 1 cc triethyl-aluminium in 30 cc n-heptane is then added. For a period of 4 hours a continuous feed of gaseous propylene is then maintained, under a constant pressure of 1000 mm Hg above atmospheric pressure.

After about 2 hours from the addition of triethyl-aluminium it can be noticed that the polymerization rate corresponds approximately to an adsorption of 11.5 g propylene per hour and per g  $\text{TiCl}_3$ .

After said period of time the product is taken out and purified as usual. In this way 42 g propylene polymer are obtained, with a high content of crystallisable product (about 80%).

#### Example 4

The autoclave of the preceding Example is charged, under a nitrogen atmosphere, with 1.05 g  $\text{TiCl}_3$  and with a solution of 3.25 g triethyl-aluminium in 250 cc n-heptane. The autoclave is then put in motion and kept for 4 hours at 70°C. The nitrogen is then replaced with propylene, saturating the solvent under a constant pressure of 1000 mm Hg above atmospheric pressure. The autoclave is kept in motion for 4 hours, while maintaining a constant propylene feed under the indicated pressure. After 2 hours the polymerization rate corresponds to the adsorption of 11.4 g propylene per hour and per g  $\text{TiCl}_3$ . The amount and structure of the obtained polymer correspond to those obtained in the preceding example.

#### Example 5

Into a 435 cc oscillating autoclave are introduced two stainless steel balls and a vial containing 1.85 g (0.012 moles) titanium trichloride, and a solution of 3.9 g tripropyl aluminium in 100 cc heptane is then added under nitrogen. The autoclave is heated to 73°C and at this temperature 90 g propylene are introduced; the autoclave is then

set in motion so as to break the vial. After 10 hours reaction at a temperature between 70 and 75°C, the reaction product is taken out; it appears as a solid very compact mass containing a large amount of adsorbed solvent. The purification is carried out by washing with diluted hydrochloride acid, as described in Examples 1 and 2. 72 g of a solid white polypropylene are obtained, which is then fractionated by extraction with hot solvents.

The acetone extract corresponds to 3.5% of the obtained polymer and is formed by oily, low molecular weight products.

The ether extract corresponds to 13.3% of the total, and is formed of a solid amorphous polypropylene, showing an intrinsic viscosity of 0.725 (in tetrahydronaphthalene at 135°C), which corresponds to a molecular weight of about 20,000.

The heptane extract corresponds to 11.4% of the total and consists of a polypropylene having an intrinsic viscosity of 0.9, i.e. a molecular weight of about 28,000. Under the X rays this fraction appears to consist of polypropylene with a crystallinity higher than 50%.

The extraction residue is 71.8% of the total, and is formed of a crystallisable, isotactic polypropylene, having an intrinsic viscosity of 3.08, i.e. a molecular weight of about 180,000. The raw polymer had therefore a total content of crystallisable polypropylene of at least 77.5%.

#### Example 6

3.7 g titanium trichloride and a solution of 9.9 g tri-*n*-butylaluminium in 250 ml heptane are introduced into a 2080 ml autoclave. 220 g of a propylene-propane mixture containing 92% propylene are added and the autoclave is heated, with stirring, to 98°C. At this temperature a rapid pressure fall takes place. The autoclave is kept in motion for 5 hours; the polymerization product is then taken out and 190 g polypropylene are obtained, which are fractionated by extraction with hot solvents, with the following results:

	% of the total polymer	Remarks
Acetone extract	11	amorphous, low-molecular weight polymer
Ether extract	20.4	solid amorphous polymers
n-Heptane extract	17.1	50% crystalline
Extraction residue	51.5	highly crystalline

The obtained polymer had therefore a crystallisability of about 60%.

#### Example 7

A 435 cc autoclave is charged with two steel balls, a vial containing 1.85 g TiCl<sub>3</sub>, a nitrogen atmosphere and a solution of 7.05 g (0.025 moles) trihexyl-aluminium in

100 cc heptane. After heating to 85°C, 92 set in motion. After keeping the temperature between 95 and 100°C for about 10 hours, the reaction product is taken out and purified in the usual way.

83 g of polypropylene are obtained, which are fractionated by extraction with hot solvents. The acetone extract corresponds to 11.8% of the total polymer and consists of oily products of low molecular weight. The ether extract is 15% of the total and consists of solid, non-crystallisable polypropylene, with an intrinsic viscosity of 0.57.

The heptane extract is 19.2% of the total and has an intrinsic viscosity of 0.8. This fraction, when examined under the X rays, shows a content of crystalline polymer higher than 50%. The extraction residue corresponds to 54% of the total and is formed by a highly crystalline, isotactic polypropylene having an intrinsic viscosity of 2.07.

The total product has therefore a content of crystallisable polypropylene of at least 64%.

#### Example 8

A 1100 cc autoclave is charged, under nitrogen atmosphere, with 1.85 g TiCl<sub>3</sub>, and with a solution in 100 cc *n*-heptane of 17.5 g of a trialkyl-aluminium having an average molecular weight corresponding to trihexadecyl-aluminium. 130 g of a propylene-propane mixture containing 91% propylene are then added. The temperature is then brought to 90°C and kept at this value for about 10 hours. The product obtained weighs, after purification, 115.2 g, and is fractionated by extraction with hot solvents.

The acetone extract, 11.4% of the total polymer, is formed of oily, low molecular weight products.

The ether extract, 19.5% of the total, is a solid, amorphous, atactic polypropylene, showing in tetrahydro naphthalene solution at 135°C an intrinsic viscosity of 0.66.

The heptane extract, 20% of the total, has a content of crystallisable polypropylene higher than 50%. This fraction has an intrinsic viscosity of 0.80.

The extraction residue, 49.1% of the total, appears, under the X rays, as a highly crystalline, isotactic polypropylene, and has an intrinsic viscosity of 3.15.

The total product has therefore a content of crystallisable polypropylene of about 59%.

#### Example 9

A solution of 10 g Al(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> in 150 ml *n*-heptane is introduced into a 1100 ml autoclave; 200 g of a propylene-propane mixture, with 92% propylene, are then added.

After heating the autoclave to 73°C, a solution of 3.8 g TiCl<sub>3</sub> in 20 ml *n*-heptane is injected.

g propylene are added and the autoclave is  
The temperature rises spontaneously to  
95°C, while the pressure falls rapidly.

The autoclave is kept in motion for about  
5 4 hours at temperatures between 80 and  
90°C. Methanol is then pumped into the

autoclave and, after purification in the  
usual way, 80 g of solid, white polypropy-  
lene are obtained, which is then fractionated  
by extraction with hot solvents.

10

The results of the fractionation are as  
follows:

	% of the total polymer	Intrinsic Viscosity	Remarks
Acetone extract	24.8	-	amorphous
15 Ether extract	36.0	0.47	solid amorphous
n-Heptane extract	18.3	0.71	50% crystallinity
Residue	20.9	1.47	highly crystalline

The raw polymer had therefore a crystallisa-  
bility of about 30%.

#### 20 Example 10

A solution of 28.2 g (1/10 of a mol) of a  
trialkyl aluminium, having an average molec-  
ular weight corresponding to trihexyl-  
aluminium, is introduced into a 2150 ml  
25 stainless steel autoclave, previously dried  
and evacuated. 285 g of liquid propylene  
are admitted, then the autoclave is put in  
motion and the heating started. Once the  
temperature of 80°C is attained, a solution  
30 of 3.8 g  $TiCl_4$  in 40 ml heptane is intro-  
duced in the reaction vessel. The tempera-  
ture goes up spontaneously reaching in a  
few minutes 120°C, and then sinks slowly  
again. When the temperature is down again

35 to 80°C, 3.8 g more of  $TiCl_4$ , dissolved in  
40 ml heptane, are added. A further tem-  
perature increase occurs although smaller  
than the previous. The autoclave is shaken  
for 2 more hours, the gaseous products are  
40 then vented and finally about 100 ml

methanol are introduced in order to decom-  
pose the polymerization agent. The resi-  
dual gases deriving from the decomposition  
of the catalyst are released, and in the auto-  
45 clave remains a viscous solid mass, which  
is discharged and purified by heating with  
ether and hydrochloric acid in order to  
remove the inorganic substances present and  
deriving from the decomposition of the  
50 catalyst. The polymer swollen by said sol-  
vents is then coagulated with methanol,  
filtered and washed with methanol. The  
solid mass left on the filter is then dried  
under reduced pressure at a temperature  
55 below 100°C. 253 g of polymer are thus  
produced, corresponding to an 87% con-  
version of the propylene employed. 73.8%  
thereof is made up of an amorphous atactic  
polymer, most of which, soluble in warm  
60 ether, having the properties of an unvul-  
canized elastomer. The ether soluble por-  
tion when extracted with warm acetone  
leaves an extraction residue having a  
softening point of 75°C, an intrinsic vis-  
cosity of 0.33 (determined in tetrahydro  
65 naphthalene solutions at 135°C) and a  
molecular weight of about 7,000.

The remaining 26.2% is formed of crys-

talline polypropylene, the bulk of which in-  
soluble in hot n-heptane, has a softening 70  
point of 150°C, an intrinsic viscosity 1.28  
and a molecular weight of about 50,000.

#### Example 11

Proceeding as in Example 10, 70.2 g of a  
trialkylaluminium having an average molec- 75  
ular weight corresponding to trihexadecyl-  
aluminium and dissolved in 500 ml heptane,  
and 350 g liquid propylene are introduced  
into a 2150 ml autoclave. The autoclave is  
heated up to 67°C while keeping it in 80  
agitation and a solution of 3.8 g titanium  
tetrachloride in 40 ml heptane is then in-  
jected under nitrogen pressure. The tem-  
perature goes up spontaneously to 110°C.

Once the temperature is down again to 85  
100°C a solution of 3.8 g titanium tetra-  
chloride in 40 ml heptane is injected once  
more. About 5 hours from the start of the  
polymerization 100 ml methanol are pumped  
into the autoclave and the residual gases 90  
are vented.

Operating as in Example 10 the catalyst  
is decomposed and after purification, 338.7  
g of a solid polymer (corresponding to  
96.5% of the propylene employed) are 95  
separated.

The raw product is made up mostly  
(83.8%) of amorphous polymer and only  
16.2% is crystalline isotactic polypropylene,  
which may be separated from the remaining 100  
polymer by means of successive extractions  
with acetone, ether and n-heptane.

The amorphous atactic portion, insoluble  
in acetone and soluble in ether, has a  
softening point of 70°C, an intrinsic vis- 105  
cosity of 0.5 and a molecular weight of  
about 11,000. The crystalline isotactic por-  
tion, insoluble in n-heptane, has a softening  
point of about 150°C, an intrinsic viscosity  
of 1.03 and a molecular weight of about 110  
37,000.

#### Example 12

A sealed glass vial containing 9 g dichloro-  
dibutoxy titanium ( $TiCl_4(OC_4H_9)_2$ ) and 3  
steel balls are introduced into a 2150 ml 115  
autoclave. Under nitrogen atmosphere a  
solution of 11.4 g triethylaluminium in 500  
ml heptane is then syphoned into the auto-  
clave. After heating up to 80°C. 275 g of

liquid propylene are then added and soon afterwards the autoclave is put in motion, keeping the temperature in the range 90-100°C. About 10 hours from the start of the polymerization methanol is pumped into the autoclave and the unreacted gases are released.

The reaction product extracted from the autoclave appears as a viscous, nearly solid, greenish brown coloured mass, which is purified as usual. After purification, 54.2 g polymer are separated, corresponding to a 20% conversion of the propylene employed. More than half (64.9%) of the obtained product is made up of amorphous atactic polypropylene, mostly soluble in warm ether.

The remainder (35.1%) is crystalline isotactic polypropylene, which may be separated from the amorphous portion by means of successive extractions with solvents.

#### Examples 13 and 14

Into an autoclave of about 2 litres capacity are introduced under nitrogen a solution of 11.4 g triethyl-aluminium in 500 cc heptane and 190 g propylene. The autoclave is heated to 64°C and at this temperature a

solution of 0.03 moles titanium tributylate monochloride in 50 cc pentane are injected under nitrogen pressure. The autoclave is kept in motion for about 8 hours at a temperature between 80 and 85°C. After this time the reaction product is taken out; after purification and drying one obtains 8 g of a solid, gummy polymer containing approximately 10% of crystalline polypropylene.

Operating in a similar way, using titanium tetrabutylate instead of the tributylate monochloride, 5.4 g of low molecular weight polypropylene are obtained, which contain only traces of crystallisable polymer.

#### Example 15

11.4 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , dissolved in 200 ml heptane and 200 g propylene are introduced, under nitrogen, into a 2150 ml autoclave. After heating with stirring to 81°C, a solution of 0.5 titanium tetraisopropylate is injected into the autoclave which is then kept in motion for about 15 hours at temperatures between 90 and 100°C. The reaction product is purified as usual, and 6 g of polymer are obtained. This is fractionated by extraction with hot solvents, in the usual way, and the following results are obtained:

	% of the total polymer	Intrinsic Viscosity	Remarks
Acetone extract	60	-	amorphous
Ether extract	33	0.37	solid amorphous
n-Heptane extract	6	0.71	50% crystallinity
Residue	1	-	highly crystalline

The obtained polymer was therefore crystallisable to the extent of about 4%.

#### Example 16

A glass vial containing 0.7 g  $\text{Ti}(\text{OH})_4$  and a solution of 5.7 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  in 150 ml n-heptane are introduced into a 435 ml autoclave filled with nitrogen. 100 g of a propylene-propane mixture containing 90% propylene are then added, the autoclave is heated to 90°C, and set in motion in order to break the vial. After 12 hours the polymerization product is taken out and the polymer is coagulated by adding methanol and acetone.

2 g of solid polymer and 35 g of semi-solid and oily, low molecular-weight products are obtained.

The solid products when examined under the X-rays reveal a crystallinity of about 50%.

#### Example 17

A glass vial containing 3.5 g titanium trichloride is introduced, together with 3 stainless steel balls, into a 2150 ml autoclave. A solution of 11.4 g triethyl aluminium in 500 ml heptane is then added under nitrogen atmosphere. The autoclave is heated to 70°C and 202 g butene, prepared from butyl alcohol and containing 70%

butene-1 and 30% butene-2, are introduced. The autoclave is kept in agitation at temperatures between 70-80°C for 20 hours. Methanol is then pumped in and the unreacted gases are discharged.

From the autoclave a very viscous-mass is discharged, which is entirely coagulated by further addition of methanol and purified as usually. 29 g of white solid polymer are obtained, which are fractionated through extraction with hot solvents. 65% of the product is crystalline, isotactic polybutene having a molecular weight of above 30,000.

The remainder is formed of a wholly amorphous, atactic product showing the properties of an unvulcanized elastomer.

When the run is repeated employing as a catalyst a mixture of  $\text{TiCl}_4$  and trihexadecyl aluminium, a viscous product is obtained which is more fluid than the one of the preceding case using  $\text{TiCl}_4$ , and is wholly amorphous, atactic polybutene.

#### Example 18

1.85 g  $\text{TiCl}_4$ , a solution of 3.9 g tripropylaluminium in 100 ml heptane, and 85 g butene-1 are introduced into a 435 ml autoclave. The polymerization is carried out at temperatures between 90 and 95°C. 60.5 g polybutene are obtained, which are frac-

tionated in the usual way.

The crystalline isotactic fraction, insoluble in hot ether, corresponds to 75% of the total product.

#### 5 Example 19

6.5 g  $\text{TiCl}_4$  in a glass vial and two steel balls are introduced into an oscillating 1100 ml autoclave. The autoclave is filled with nitrogen and a solution of 19.8 g  $\text{Al}(\text{n-C}_4\text{H}_9)_3$  in 500 ml n-heptane is then added. After heating to 85°C, 115 g

butene-1 (pure grade) are added and the autoclave is put in motion so as to break the vial. The temperature rises rapidly to 95°C. After keeping the autoclave in 15 motion for 4 hours, the polymerization product is taken out and purified as usual. 109 g white, solid polybutene of fibrous appearance is obtained, and is fractionated by extraction with hot solvents. The fractions 20 are as follows:

	% of the total polymer	Intrinsic Viscosity	Remarks
Acetone extract	3.1	-	Low molecular weight, oily polymers
25 Ether extract	29.2	0.82	amorphous solid
n-Heptane extract	67.7	2.12	crystalline

#### Example 20

A solution of 8 g tripropyl aluminium in 90 ml n-heptane and 47 g butene-1 (pure 30 grade) are introduced into a 435 ml autoclave. The autoclave is heated to 65°C, and a solution of 3.8 g titanium tetrachloride in 30 ml n-heptane is injected under nitrogen pressure. The temperature rises spontan-

eously to about 75°C. The autoclave is then 35 kept in motion for about 5 hours, at temperatures between 75 and 85°C.

22 g of a white, solid polybutene are obtained after purification in the usual way. These are fractionated by extraction with 40 hot solvents, and the following results are obtained:

	% of the total polymer	Intrinsic Viscosity	Remarks
45 Acetone extract	20	-	Low molecular weight polymers
Ether extract	43.2	0.535	amorphous solid
n-Heptane extract	36.8	1.07	highly crystalline

#### Example 21

A solution of 19.8 g  $\text{Al}(\text{n-C}_4\text{H}_9)_3$  in 450 50 ml n-heptane is introduced into a 1100 ml autoclave filled with nitrogen. After adding 80 g butene-1 (pure grade) the autoclave is heated to 85°C, and at this point a solution of 7.6 g  $\text{TiCl}_4$  in 50 ml n-heptane is injected. 55 The temperature goes up rapidly by about

10°C while the pressure falls. The autoclave is then kept in motion for about 4 hours at temperatures between 85 and 95°C.

After purification in the usual way the polymerisation product yields 44.2 g poly- 60 butene, which is fractionated by extraction with hot solvents, with the following results:

	% of the total polymer	Intrinsic Viscosity	Remarks
65 Acetone extract	12.4	-	-
Ether extract	40.3	0.28	solid, amorphous
Residue	47.3	0.98	highly crystalline completely soluble in n-heptane

#### Example 22

70 A glass vial containing 8 g titanium trichloride and 3 steel balls are introduced into a 2150 autoclave. A solution of 12 g diethyl aluminium monochloride in 500 ml n-heptane is then introduced under nitrogen. 75 After heating to 76°C, 365 g of technical propylene (85% propylene) are added. Soon afterwards the autoclave is shaken to cause the breakage of the  $\text{TiCl}_4$  vial. Agitation is continued, at temperatures in 80 the range 80-90°C; when a temperature decrease is no longer observed the gases are released and (while operating as in example

2) 235 g of polymer are obtained, corresponding to a 75% conversion of the propylene employed. The obtained product is 85 made up mostly (84%) of crystalline isotactic propylene, which can be separated from the non-crystalline products by extraction with solvents.

#### Example 23

90 A glass vial containing 7 g  $\text{TiCl}_4$  and 3 stainless steel balls are introduced into a 2080 ml stainless steel autoclave in nitrogen atmosphere. A solution of 1.6 g (0.013 moles)  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  in 500 ml n-heptane is then 95 added. After heating to 70°C, 350 g propy-

lene are injected into the autoclave which is set in motion, thereby breaking the glass vial. After 10 hours at temperatures between 80 and 85°C, during which a continuous pressure fall is observed, the residual gases are vented and 10 ml propylene are recovered.

The solid polymer obtained weighs, after purification in the usual way, 315 g.

10 The extract with hot acetone is 10.8% of the total polymer. The ether extract, 16.2% of the total, is an amorphous, solid atactic polypropylene, with an intrinsic viscosity of 0.43. The n-heptane extract, 15 9.6% of the total, has an intrinsic viscosity of 0.955, and has a crystallinity, as detected by X-rays measurements, higher than 50%. The extraction residue, 63.4% of the total polymer, is a highly crystalline isotactic 20 polypropylene, with an intrinsic viscosity of 2.05.

#### Example 24

Into an oscillating autoclave of 1100 cc capacity are introduced two steel balls and 25 a glass vial containing 1.85 g  $\text{TiCl}_3$ . Under nitrogen atmosphere a solution of 4.95 g tri-*iso*-butyl-aluminium in 100 cc heptane is then added. The autoclave is heated to 85°C; at this temperature 100 g propylene 30 are introduced, and the autoclave is set in motion. After about 10 hours at temperatures between 70 and 75°C, during which a considerable pressure decrease is observed, the product is taken out and treated as

	% of the total polymer	Intrinsic Viscosity	Remarks
70 Acetone extract	18.7	-	oily, low molecular weight polymers
Ether extract	43	0.41	amorphous solid
n-Heptane extract	19	0.76	50% crystallinity
Residue	19.3	1.87	crystalline

The raw polymer had therefore a crystalli-  
75 sability of about 29%.

#### Example 26

Example 10 is repeated, with the excep-  
tion that a 435 ml autoclave is employed, wherein 20 g (1/20 mol) of a dialkylalu-  
80 minium monochloride, having an average molecular weight corresponding to didodecylaluminium monochloride, dissolved in 75 ml anhydrous benzene, and 120 g liquid propylene are introduced. The autoclave is  
85 heated up to 72°C while agitating and then a solution of 1.9 g titanium tetrachloride in 20 ml heptane is injected under nitrogen pressure. A spontaneous temperature increase of several degrees occurs. A solution  
90 of 1.9 g titanium tetrachloride in 20 ml gasoline is again injected. About 10 hours from the start, the catalyst is decomposed with methanol as in example 10, and 68.5 g of solid polymer are obtained, correspond-  
95 ing to a 57% conversion of the employed

usual.

65.6 g polypropylene are obtained, which are fractionated by extraction with hot solvents. The acetone extract corresponds to 5.1% of the total, the ether extract to 27.4% and consists of a solid, amorphous 40 atactic polypropylene, with an intrinsic viscosity of 0.895. The heptane extract corresponds to 14.9% of the total, and consists of polypropylene which is crystalline to the extent of more than 50%, and has, in 45 tetrahydro naphthelene solution at 135°C. an intrinsic viscosity of 1.17. The residue is 52.6% of the total and consists of a highly crystalline, isotactic polypropylene, having an intrinsic viscosity of 2.56. 50

The product obtained has therefore a content of crystallisable polypropylene of at least 60%.

#### Example 25

A solution of 19.8 g  $\text{Al}(\text{i-C}_4\text{H}_9)_3$  in 500 55 ml n-heptane and 290 g propylene are introduced into a 2150 ml autoclave filled with nitrogen. After heating to 66°C, a solution of 7.6 g  $\text{TiCl}_4$  in 80 ml n-heptane is injected. The temperature rises sharply to 60 95°C. After keeping the autoclave in motion for about 7 hours at this temperature, the product is taken out and purified as usual. 215 g of solid polymer are obtained which are fractionated by extraction 65 with hot solvents. The results of the fractionation are as follows:

propylene. The polymer consists practically in its entirety (more than 90%) of amorphous atactic product. The acetone insoluble and ether soluble portion of the amorphous polymer has a softening point of 100 55°C, an intrinsic viscosity of 0.25 and a molecular weight of about 5,000.

#### Example 27

3.4 g titanium tribromide and a solution of 2.85 g triethylaluminium in 100 ml 105 n-heptane are introduced into a 435 ml autoclave. 115 g of a propylene-propane mixture, with 91% propylene, are then added. The autoclave is heated to 80-90°C and kept in motion for about 10 hours. The 110 polymerization product is purified as in the previous Examples and 102 g of a solid polymer are obtained, which is fractionated by extraction with hot solvents.

The acetone extract, 10% of the total, 115 consists of oily, low molecular weight polymers. The ether extract, 36% of the total,



is a solid, amorphous atactic polypropylene. The n-heptane extract, 20% of the total, has a crystallinity, as detected by X-rays measurement, higher than 50%. The extraction residue, 34% of the total, is a highly crystalline isotactic polypropylene.

The obtained polymer had therefore a crystallisability of at least 44%.

#### Example 28

5.15 g  $\text{TiI}_3$  and a solution of 2.85 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  in 100 ml heptane are charged into a 435 ml autoclave. 130 g of a propylene-propane mixture, containing 91% propylene, are then added, the autoclave is heated to 85-90°C and kept in motion for about 20 hours.

The polymerisation product appears as a semi-solid tacky mass, which is purified and coagulated with methanol. 30 g solid, white polypropylene are thus obtained, while the evaporation of the solvent used in the polymerisation and purification steps yields 54.3 g oily, low molecular weight products. Of the total 84.3 g of product, 64.5% is thus formed of oily products.

The solid polymer is fractionated by extraction with hot solvents. The amount of crystalline isotactic polypropylene thereby obtained is 10% of the total polymer.

#### Example 29

Into a 435 ml autoclave two steel balls (1 inch diameter) and a glass vial containing 3.2 g (i.e. 0.02 moles) of solid vanadium trichloride are introduced. Then a solution of 5.7 g triethyl aluminium in 100 ml n-heptane is added under nitrogen. The autoclave is heated to 81°C and 98 g pure liquid propylene are introduced; thereafter shaking of the autoclave is started, and continued for about 10 hours at temperatures in the range 81 to 90°C, while a steady, regular pressure decrease may be noticed. After said time 50 ml methanol are pumped into the autoclave and 6 Nl of gas are collected. A solid, compact polymer is discharged from the autoclave. It is first broken up in small pieces and then treated with warm ether and hydrochloric acid and finally coagulated with methanol and filtered. Since warm ether does not appreciably swell the obtained polymer, a further purification of the polymer is necessary, by treating it with warm benzene (whereby it will be entirely swollen) and hydrochloric acid. The polymer is then coagulated with methanol and acetone, filtered, washed and dried by heating it under vacuum, to obtain 64 g of a solid white product. The polymer obtained is fractionated as in the preceding Example.

The acetone extract is 12.6% of the polymer obtained and is formed of low molecular weight amorphous polymers. The ether extract, 21.4% of the total, is formed of amorphous atactic polypropylene with an

intrinsic viscosity of 0.55. The heptane extract, 24.1% of the total, has more than 50% crystallinity (by X-ray examination). This fraction has an intrinsic viscosity of 0.85, i.e. a molecular weight of about 25,000. The extraction residue is a highly crystalline isotactic polypropylene having an intrinsic viscosity of 1.78, corresponding to a molecular weight of about 80,000.

The raw polypropylene obtained had therefore a content of crystallisable polymer of at least 54%.

#### Example 30

A solution of 11.4 g triethyl-aluminium in 400 cc n-heptane, and 350 g of a mixture containing 82% propylene and 18% propane are introduced, under nitrogen, into an autoclave of 2000 cc capacity. The autoclave is heated with stirring to 80°C, and at this temperature a solution of 6.8 g  $\text{VOCl}_3$  in 100 cc n-heptane is injected. The temperature rises spontaneously to 87°C, while the pressure falls rapidly. After about 5 hours methanol is pumped into the autoclave and the polymerization product is taken out. The product is purified from the inorganic compounds present by heating with ether and hydrogen chloride and then complete coagulation with methanol. 172.5 g polypropylene are obtained, corresponding to 60% of the propylene used. The polymer is then fractionated by extraction with hot solvents.

The acetone extract, 29% of the obtained polymer, is an amorphous, low molecular weight polypropylene. The ether extract, 29.4% of the total, is an amorphous atactic polypropylene with an intrinsic viscosity of 0.52. The heptane extract, having a crystallinity by X-rays of about 50%, has an intrinsic viscosity of 1.15. The extraction residue appears under the X-rays as a highly crystalline isotactic polypropylene, and has an intrinsic viscosity of 2.1.

The raw polymer obtained had therefore a crystallisability of approximately 32.4%.

#### Example 31

Into a stainless steel shaking autoclave of 435 ml capacity 2 stainless steel balls (1 inch diameter) and a vial containing 3.25 g  $\text{CrCl}_3$  (i.e. 0.02 moles) are introduced. Into the closed autoclave a solution of 5.7 g (i.e. 0.05 moles) triethyl aluminium in 100 ml n-heptane is then added under nitrogen. The autoclave is then heated without shaking to 80°C and 115 g pure liquid propylene are introduced. Soon after, shaking is started and continued at temperatures in the range 80 to 110°C. 40 hours from the start the unreacted propylene is discharged. The reaction product is purified from the catalyst by washing with methanol and hydrochloric acid, and the solvents evaporated. The obtained polymer is extracted with ether, which dissolves 37% of it; the

dissolved fraction is completely amorphous. In the subsequent extraction with boiling heptane a fraction corresponding to 44% of the total is dissolved, which is 50% crystalline and has an intrinsic viscosity of 0.42.

The extraction residue is a crystallisable isotactic material and has an intrinsic viscosity of 0.765. The crude product has therefore a content of crystallisable polymer of approximately 41%.

#### Example 32

5.7 g triethyl aluminium dissolved in 200 cc heptane and 172 g propylene are charged under nitrogen into a 1100 cc autoclave. The autoclave is heated to 80°C and at this temperature a solution of 0.75 g chromium oxychloride in 50 cc heptane is injected. After keeping the autoclave in motion for about 20 hours the product is taken out and only small amounts of a propylene polymer, containing about 21% of crystalline, isotactic product, are isolated.

#### Example 33

A glass vial containing 2.36 g (0.012 moles)  $ZrCl_4$ , a solution of 2.85 g triethyl aluminium in 100 cc n-heptane, and two steel balls are charged into a 435 cc shaking autoclave under nitrogen atmosphere. The autoclave is heated, while stationary, to 73°C and at this temperature 70 g of a propylene-propane mixture containing 91% propylene is then added; the autoclave is set in motion thereafter so as to break the vial. After a few hours at 80°C 7.6 g of polymer are obtained which are fractionated by extraction with hot solvents.

By extraction with hot ether the amorphous, atactic polypropylene, about 30% of the total product, is dissolved. In the subsequent extraction with heptane, 10% of the product is dissolved, this fraction being a polypropylene which is crystallised to the extent of more than 50%. The extraction residue is a highly crystalline, isotactic polypropylene.

The raw product contains therefore about 65% of crystallisable polypropylene.

#### Example 34

A glass vial containing 9 g  $WCl_6$  and two steel balls are introduced into a 2080 ml oscillating autoclave. The autoclave is then filled with nitrogen and a solution of 11.4 g  $Al(C_2H_5)_3$  in 500 ml n-heptane is added. After heating to 70°C, 340 g of a propylene-propane mixture containing 90% propylene is added and the autoclave is set in motion. After about 10 hours at 90-95°C the polymerization product is taken out. It appears as a liquid brown mass. After washing with acid and evaporation of the solvent, 38 g of oily products and 0.5 g of solid polymer are obtained. The solid product has approximately 50% crystallinity when examined under the X-rays.

#### Example 35

Into a 435 ml autoclave two steel balls and a glass vial containing 3.2 g of solid vanadium trichloride are introduced. Operating as in the foregoing Examples 5.7 g (i.e. 0.05 moles) triethyl aluminium dissolved in 100 ml heptane are then added. The autoclave is then heated to 83°C, 110 g of a mixture of butene-1 and butene-2 with 70% of butene-1 are introduced, and the autoclave is shaken to break the vial. After about 10 hours of shaking at temperatures in the range 86 to 96°C, the autoclave is discharged, operating as in the foregoing Examples.

42 g of a solid, fibrous, white substance are obtained; 21.5 g thereof (i.e. 51.3%) can be extracted with ether and appear substantially amorphous under the X-rays. The extraction residue, corresponding to 48.7% of the whole solid polymer, has an intrinsic viscosity of 1.1 and when examined under the X-rays, has high crystallinity.

#### Example 36

A solution of 11.4 g triethyl-aluminium in 400 cc heptane is introduced under nitrogen into an autoclave of about 2 litres capacity. 220 g of a mixture of butene-1 and butene-2 containing 70% of the former is then added. The autoclave is heated to 75°C and at this temperature a solution of 7.7 g  $VCl_3$  in 100 cc pentane is added. The autoclave is kept in motion for about 10 hours at temperatures between 75 and 80°C; the reaction product is then taken out and purified as usual, obtaining 90.2 g polybutene which are fractionated by extracting in succession with hot acetone and ethyl ether. The residue after the extraction with ether corresponds to 27.8% of the polymer obtained and is formed by polybutene which shows crystallinity under the X-rays. This fraction has an intrinsic viscosity, in tetrahydronaphthalene solution at 135°C, of 1.65.

#### Example 37

Into a 2150 ml autoclave 2 steel balls and a vial containing 9.5 g (i.e. 0.044 moles)  $ZrCl_4$  are introduced. The autoclave is then evacuated and a solution of 45 g (i.e. 0.1 moles) of a trialkyl aluminium compound (of an average molecular weight corresponding to tridecyl aluminium) in 450 ml anhydrous benzene is added. The autoclave is heated, without shaking to 82°C and 222 g propylene are introduced. Soon after shaking is started, to break the vial, and continued for 14 hours at temperatures in the range 82 to 118°C, while a steady pressure decrease is noticed. After that time 100 ml methanol are pumped in and a reaction product very much swollen with benzene is discharged. The product obtained contains, a high proportion of relatively low molecular weight polymers which are amorphous, whereas only 12% of the total is

insoluble in ether.

*Example 38*

8 g  $Al(C_2H_5)_3$ , dissolved in 200 ml heptane and 200 g of a propylene-propane mixture containing 91% propylene are introduced into a 1100 ml autoclave filled with nitrogen. After heating to 82°C, 3.85 g  $VC_2Cl_3$ , dissolved in 50 ml n-heptane are injected under nitrogen pressure. The temperature goes up rapidly to 100°C, while a fall of pressure can be noticed. The autoclave is kept in motion for about 5 hours

at a temperature between 90 and 100°C.

The polymerisation product is then taken out; it appears as a compact solid mass swollen by the solvent. The product is purified by washing with solvents acidified with hydrogen chloride and then completely coagulated with methanol. 150.8 g of a solid, white polymer are obtained, which are fractionated by extraction with hot solvent. The results of the fractionation are as follows:

		% of the total polymer	Intrinsic Viscosity	Remarks
25	Acetone extract	10	-	-
	Ether extract	35.8	0.52	-
	n-Heptane extract	26.5	1.3	50% crystallinity
	Residue	27.7	2.58	crystalline, mol. wt. about 140,000

30 The polymerization product had, therefore, a content of approximately 41% crystallisable polymer.

*Example 39*

Into a 435 ml autoclave two steel balls and a vial containing 3.3 g (i.e. 0.012 moles)  $CrCl_3$  are introduced, and then under nitrogen atmosphere, a solution of 22.5 g of a trialkyl aluminium compound, having an average molecular weight corresponding to tridecyl aluminium, in 80 ml anhydrous benzene. The autoclave is heated without shaking to 89°C and 100 g propylene are then admitted. Soon after, shaking is started and maintained for 14 hours at temperatures in the range 89 to 105°C. The purification and separation of the polymer is then carried out as in the preceding examples. The polymer, which is richer in products of a lower molecular weight, contains only 14% of products insoluble in ether, and extractable with hot heptane. When examined under the X-rays this fraction appears approximately as 50% crystalline.

*Example 40*

Into a 2350 ml autoclave 2 steel balls and a vial containing 7.8 g of liquid  $VC_2Cl_3$  are introduced. The solution of 45 g of a trialkyl aluminium (of an average molecular

weight corresponding to aluminium tridecyl) in 500 ml n-heptane is then added. The autoclave is then heated to 87°C and 260 g of butenes (containing about 70% of butene-1) are added. Shaking of the autoclave is then started and continued for about 10 hours, while keeping the temperature near 87°C.

Operating as in the foregoing Examples, 113 g of a butene-1 polymer are obtained which is found to be almost entirely amorphous. It contains in fact less than 10% of crystallisable product.

*Example 41*

A solution of 17.5 g  $Al(C_2H_5)_3$  in 200 ml n-heptane is introduced into a 2080 ml autoclave filled with nitrogen. 280 g of a propylene-propane mixture containing 91% propylene are then added. After heating to 80°C, 2.2 g  $VOCl_3$ , dissolved in 50 ml heptane are injected under nitrogen pressure. The temperature rises sharply to 90°C, while the pressure falls. After keeping the autoclave in motion for about 5 hours, the product is taken out and purified as usual. By coagulation with a large amount of methanol 90 g of polypropylene are obtained, which are fractionated by extraction with hot solvents. The following fractions are obtained:

		% of the total polymer	Intrinsic Viscosity	Remarks
90	Acetone extract	47.6	-	-
	Ether extract	31.5	-	amorphous solid
	n-Heptane extract	11.8	-	50% crystallinity
	Residue	9.1	-	crystalline

95 The obtained polymer had, therefore, a content of approximately 15% crystallisable polymer.

*Example 42*

7.6 g of  $TiCl_4$ , dissolved in 20 ml n-heptane are added to 11.4 g triethyl aluminium dissolved in 50 ml n-heptane, at 70°C, while stirring. The reaction mixture

is then filtered under nitrogen atmosphere through a porous diaphragm (diameter of the pores 5-15 microns) and the solid phase is washed on the filter with a total of 120 ml of an heptane solution containing 2% of triethyl aluminium. The solid phase is then suspended in 100 ml n-heptane and introduced, while stirring under nitrogen pres-

sure, into a glass vial which is then sealed. The vial, together with 3 steel balls (1 inch diameter), and a solution of 11.4 g triethylaluminum in 400 ml n-heptane are then introduced into a 150 autoclave. The autoclave is heated to 80°C and 295 g liquid propylene are introduced, the autoclave being soon after put in motion, while the temperature is kept between 80° and 90°C; when a pressure decrease no longer occurs, methanol is pumped into the autoclave and the gaseous products are released.

The reaction product is extracted from the autoclave as an almost entirely solid mass which is purified by the usual methods and by treatment with boiling toluene and concentrated HCl. After precipitation with methanol and several washings with methanol it is filtered and dried. 111 g of polymer are thus obtained, which corresponds to a 37.5% conversion of the propylene employed. More than half of the product (53.7%) is made up of crystallisable polypropylene, which may be separated from the non-crystalline product by extraction with solvents.

#### Example 43

80 ml of the solution obtained by filtering the catalyst used in the foregoing example are syphoned into a 310 ml autoclave under nitrogen atmosphere. The autoclave is heated up to 80°C, 76 g liquid propylene are introduced and finally the autoclave is put in agitation. About 6 hours from the start of the polymerization when a remarkable pressure decrease is no longer observed, methanol is pumped into the autoclave in order to decompose the catalyst, and the gaseous products are then vented. The reaction product extracted from the autoclave appears as a viscous, nearly colourless liquid; it is coagulated with methanol to obtain a solid, gummy product which is purified as usual. It appears wholly amorphous under the X-rays.

#### Example 44

To a solution of 11.4 g triethyl aluminium in 70 ml heptane a solution of 7.6 g titanium tetrachloride in 20 ml heptane is added, while stirring, at a temperature of 70°C. A black precipitate is formed while gas is evolved. The precipitate is filtered off under nitrogen pressure on a porous diaphragm (pores diameter 5-15 microns) and then repeatedly washed with heptane containing 2% of triethylaluminium. The black precipitate is then suspended in 250 ml heptane containing 11.4 g triethylaluminium. The whole is syphoned under nitrogen atmosphere into a 1000 ml, three-neck flask fitted with a stirrer. The flask is heated to 65°C and 150 g styrene are added. The mixture is kept in agitation for 2½ hours at a temperature in the range 70-75°C. The mixture obtained is then cooled and poured

into methanol in order to decompose the catalyst. The inorganic products are then dissolved by treating with hydrochloric acid. The reaction mixture separates into two layers of which the upper is heptane containing in suspension the flocky, easily filterable polymer.

The precipitate is filtered and purified by boiling with acetone containing some hydrogen chloride, filtering and repeated washing with acetone. During such operation no loss in weight is practically observed.

The obtained product has high crystallinity under the X-rays and starts melting above 210°C.

#### Example 45

7.3 g vanadium tetrachloride dissolved in 20 ml n-heptane are added at 70°C, while stirring, to 11.4 g of triethyl aluminium dissolved in 70 ml n-heptane. The reaction mixture, consisting of a liquid phase wherein a brown precipitate is in suspension, is filtered under nitrogen atmosphere through a porous diaphragm whose pores have a diameter of 5 to 15 microns. The solid phase is then washed three times on the filter with 30 ml each time of a 1% solution of triethyl aluminium in n-heptane. The solid phase is then suspended in 250 ml n-heptane, and, while stirring, it is syphoned under nitrogen atmosphere into a previously de-aerated glass flask provided with a stirrer, dropping funnel and refluxing cooler. Into the flask kept under nitrogen atmosphere, 11.4 g triethyl aluminium are then added. The temperature of the mixture is raised to 70°C and 150 g styrene are added while stirring. Agitation is maintained for 4 hours at temperatures between 70 and 75°C. The flask is then allowed to cool, the catalyst is decomposed with methanol and finally the reaction product is treated with hydrochloric acid.

The liquid mass contains in suspension a solid, flocky polymer which is then separated by filtration.

The solid polymer is made up of two portions, one of which is soluble, the other insoluble in acetone. The insoluble portion, corresponding to 68% of the whole solid, is found to be highly crystalline (isotactic), whereas the acetone soluble portion is amorphous (atactic).

#### Example 46

The filtered solution, described in the foregoing Example on the preparation of the catalyst, is introduced into a 1000 ml flask under nitrogen. 100 ml n-heptane are then added and the flask is heated to 80°C. Next 150 g styrene are added while stirring. The agitation is continued for 4 hours at temperatures in the range 70 to 75°C. After cooling, the reaction product is treated with methanol and hydrogen chloride. Small amounts of styrene polymer (entirely amorphous) are separated from the methanol

solution. It is shown thereby that while the little dispersed catalyst, which may be separated by filtration as indicated in Example 42, yields a prevailingly crystallisable product, the dispersed portion (which passes through the filter) yields a wholly amorphous atactic polymer.

We are aware of a proposed process to copolymerise ethylene with another ethylenically unsaturated hydrocarbon monomer in which the ethylene is polymerised to a solid polymer having a melt index within the range of 0.005 to 3 and wherein ethylene is continuously added to a reaction zone in which it is polymerised in an inert liquid hydrocarbon solvent at a temperature within the range 150°C to 230°C and under a pressure sufficient to maintain appreciable concentration of ethylene in the solvent and in the presence of a titanium-containing complex as catalyst and we make no claim to the said proposed process nor do we make any claim herein to any method claimed in claim 19 or claim 22 of the specification of our Letters Patent No. 810023 but

#### WHAT WE CLAIM IS:—

1. A method of polymerising an alpha-olefin having at least three carbon atoms which satisfies the general formula  $R-CH=CH_2$  (where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group) to form a linear, essentially unbranched, head-to-tail polymer by the use as a catalyst of a compound of a metal of Group IVa, Va or VIa as hereinbefore defined, in contact with metal-alkyl groups containing aluminium or a metal of Group II as hereinbefore defined, at least a part of the metal of Group IVa, Va or VIa being present in the catalyst in a valency state lower than the maximum, wherein the crystallisable or non-crystallisable content of the polymerisate is selectively regulated towards an increased crystallisable or non-crystallisable content, as the case may be, by the respective use in the polymerisation process of a said catalyst in the wholly or substantially wholly solid form, or in the wholly or substantially wholly non-solid form, the appropriate form resulting either directly from a suitable choice of starting materials and conditions of formation or from an intermediate step of preparation to produce a catalyst having a selected proportion of the solid to the non-solid form, the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen free state polymerisation of the said olefin to a linear, essentially unbranched, head-to-tail polymer results.

2. A method according to claim 1 in which the formation of the catalyst includes the step of contacting an appropriate organo-metallic compound of a metal of Group II of the Periodic Table as herein

defined or of aluminium with a compound of a metal of Group IVa, Va or VIa of the said Table.

3. A method according to claim 2 in which the compound of the metal of Group IVa, Va or VIa has a valency less than four and is crystalline and insoluble in the olefin to be polymerised or the solvent therefor.

4. A method of polymerising an alpha-olefin having at least three carbon atoms which satisfies the general formula  $R-CH=CH_2$  (where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group), to a linear, essentially unbranched, head-to-tail polymer wherein the polymerisation is effected in the presence of a catalyst formed by contacting a crystalline compound of a metal of Group IVa, Va or VIa as hereinbefore defined which has a valency less than four and is substantially insoluble in the polymerisation medium with an alkyl compound of a metal of Group II or of aluminium, said alkyl group containing not more than 4 carbon atoms, the choice of the constituents of the catalyst and the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen-free state polymerisation of the said olefin to a linear, essentially unbranched, head-to-tail, predominantly to substantially crystalline or crystallisable polymer results.

5. A method according to either of claims 1 or 2 in which the catalyst is divided into fractions of solid and non-solid form or into fractions of differing proportions of solid to non-solid form by filtration, decantation, sedimentation, centrifuging or flotation, and the fraction containing the solid or the greater amount of solid form is used as catalyst.

6. A method according to any one of claims 1 to 4, in which said compound of the metal of Group IV, Va or VIa is an halide of trivalent titanium, zirconium or vanadium.

7. A method according to claim 6 in which said compound of the metal of Group IVa, Va or VIa is titanium trichloride, zirconium trichloride or vanadium trichloride.

8. A method according to any one of claims 1 to 4 in which said compound of the metal of Group IVa, Va or VIa is titanium dichloride.

9. A method according to any one of claims 2 to 8, in which aluminium triethyl is employed.

10. A method according to any one of claims 2 to 9 in which after the initial quantity of the compound of Group IVa, Va or VIa and the alkyl compound have been contacted further alkyl compound is added.

11. A method according to claim 1 or claim 2 in which the catalyst is divided into

- fractions of solid and non-solid form or into fractions of differing proportions of solid to non-solid form by filtration, decantation, sedimentation, centrifuging or flotation, and the fraction containing the non-solid or the greater amount of non-solid form is used as catalyst.
12. A method according to claim 1 or claim 11 in which the formation of the catalyst includes the step of reacting an organo-metallic compound of a metal of Group II of the said Table or of aluminium with a liquid or dissolved compound of a metal of Group IVa, Va or VIa of the said Table.
13. A method according to any one of claims 1, 11 or 12, in which at least one of the reactive components used in forming the catalyst contains lyophilic groups.
14. A method according to claim 13 in which the compound of a metal of Group II of the said Table or of aluminium contains alkyl groups with more than 4 (preferably 6 to 16) carbon atoms.
15. A method according to claim 13 in which the lyophilic groups are or include alkoxy groups.
16. A method according to any one of claims 1 and 11 to 15, in which the compound of a metal of Group IVa, Va or VIa of the said Table is an halide, oxyhalide, alkoxyhalide or alkoxide of titanium, zirconium or vanadium.
17. A method of polymerising an alpha-olefin according to the method of any preceding claim in which R is in linear alkyl group containing not more than 3 carbon atoms.
18. A method of polymerising propylene according to the method claimed in any one of claims 1 to 17.
19. A method of polymerising butene-1 according to the method claimed in any one of claims 1 to 17.
20. A method of polymerising styrene according to the method claimed in any one of claims 1 to 16.
21. A method of polymerising propylene to form a linear, essentially unbranched, head-to-tail polymer which is predominantly to substantially crystalline (or crystallisable) by the use as a catalyst of solid, titanium trichloride, zirconium trichloride, vanadium trichloride or titanium dichloride, contacted with an aluminium alkyl compound containing not more than 4 carbon atoms, the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen-free state polymerisation to a linear, essentially unbranched, head-to-tail polymer results.
22. A method of polymerising butene-1 to form a linear, essentially unbranched, head-to-tail polymer which is predominantly to substantially crystalline (or crystallisable) by the use as a catalyst of solid titanium trichloride, zirconium trichloride, vanadium trichloride or titanium dichloride, contacted with an aluminium-alkyl compound containing not more than 4 carbon atoms, the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen-free state polymerisation to a linear, essentially unbranched, head-to-tail polymer results.
32. A method of polymerising styrene to form a linear, essentially unbranched, head-to-tail polymer which is prevailingly to substantially crystalline (or crystallisable) by the use as a catalyst of solid titanium trichloride, zirconium trichloride, vanadium trichloride or titanium dichloride, contacted with an aluminium-alkyl compound containing not more than 4 carbon atoms, the conditions of polymerisation being in all other respects such that in a substantially anhydrous and oxygen-free state polymerisation to a linear, essentially unbranched, head-to-tail polymer results.
24. A method of polymerising an alpha-olefin substantially as hereinbefore described with reference to any one of the foregoing Examples.
25. A polymer which is produced by a method claimed in any one of the preceding claims.
26. A catalytic compound useful in a method of polymerising alpha-olefins according to any one of claims 1 to 4, 6 to 10 and 21 to 23 to obtain predominantly to substantially crystalline or crystallisable polymers which is obtained by contacting a solid compound of valency less than 4 of a metal of Group IVa, Va or VIa as hereinbefore defined with an organo-metallic compound.
27. A catalytic compound useful in a method of polymerising alpha-olefins according to any one of claims 1 to 10 and 21 to 23 to obtain predominantly to substantially crystalline (or crystallisable) polymers which is obtained by contacting titanium trichloride with aluminium triethyl.
28. A crude unfractionated polymerisate obtained by polymerising propylene in which more than half but not substantially the whole of the polymerisate is crystallisable and is non-extractable with boiling *n*-heptane.
29. Crystalline or crystallisable polypropylene obtained by separation from a polymerisate according to claim 28.

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Reference has been directed, in pursuance of Section 8 of the Patents Act, 1949, to Specification No. 810,023.

828,791

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of the Original on a reduced scale.*

